

Catalytic Properties of Aluminum/Nickel-, Copper-Containing Oxide Film Compositions

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Abstract—The possibility of the single-step formation of nickel- and copper-containing thin-film oxide systems on aluminum by plasma electrolytic oxidation was demonstrated. The resulting structures were found to be active in the reaction of CO oxidation to CO₂ in the temperature region 300–500°C. However, the resulting structures exhibited stable catalytic activity only in the simultaneous presence of nickel and copper compounds. The films were studied using X-ray diffraction, X-ray spectroscopic analysis, X-ray photoelectron spectroscopy, and electron microscopy. The resulting films exhibited an essentially inhomogeneous composition through the thickness. Electrolyte elements such as nickel, copper, sodium, and phosphorus were concentrated at the surface. Nickel occurred as Ni²⁺, and copper occurred as Cu⁺ and Cu²⁺. The surface contained carbon in detectable amounts.

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INTRODUCTION

Catalysts on metal supports are characterized by high thermal conductivity and mechanical strength. Because of this, supports based on aluminum with an oxide film are finding increasing use [1–4]. Aluminum/oxide layer compositions are prepared by various techniques [1], including the traditional anodic oxidation of aluminum in acid and alkali solutions [1, 2] and the oxidation of aluminum at spark and arc discharge voltages in aqueous salt solutions (anodic spark oxidation, microarc oxidation, or plasma electrolytic oxidation (PEO)–deposition) [3, 4]. The PEO process allows one to generate both ceramiclike layers of the oxide of the treated metal and multiphase surface structures, which include compounds based on solution components. The complex composition of PEO structures results from high-temperature interactions initiated in the vicinity of electric discharge channels at the film/electrolyte interface. Because of this, the PEO process is promising for the direct preparation of catalytically active metal/multiphase surface film compositions. Relevant publications are currently available [5–7].

Rudnev et al. [5] found that Mn_xO_y/TiO₂/Ti compositions formed using the PEO process were highly competitive with manganese oxide systems on titanium prepared by a traditional roasting technology. The PEO structures on aluminum, titanium, and magnesium, which contained nickel, chromium, and molybdenum compounds along with Al₂O₃, TiO₂, and MgO, were active in the oxidative dehydrogenation of

cyclohexane [6]. The PEO layers on aluminum with Al₂O₃ and copper, manganese, and tungsten compounds exhibited catalytic properties toward catalytic cracking reactions [7].

It is well known [8–11] that copper and nickel oxides are catalysts for redox reactions. The aim of this work was to prepare nickel- and/or copper-containing PEO layers on aluminum and to study their composition and catalytic properties in the reaction of CO oxidation to CO₂.

EXPERIMENTAL

An aqueous electrolyte containing 0.066 M Na₃PO₄ + 0.034 M Na₂B₄O₇ + 0.006 M Na₂WO₄ (henceforth referred to as PBW [12]) was chosen for the formation of PEO layers on the AMg5 aluminum alloy because it allowed us to form corrosion-resistant layers containing γ-Al₂O₃. Moreover, insoluble transition metal compounds, including hydroxides, are precipitated on the introduction of transition metal salts into alkaline electrolytes like PBW; this is of importance for the preparation of multiphase oxide structures on treated metal surfaces in the course of PEO [13]. To obtain PEO layers with nickel and/or copper compounds, 0.08 mol/l Ni(CH₃COO)₂ and/or 0.025 mol/l Cu(CH₃COO)₂ were introduced into the PBW electrolyte (the corresponding electrolytes are referred to as PBW_{Ni}, PBW_{Cu}, and PBW_{NiCu}, respectively, in the text). The concentration ratio between the nickel and copper salts was chosen

Table 1. Effect of electrolyte on the elemental composition (according to X-ray spectroscopic analysis data), phase composition, and thickness (h) of films formed by anodic polarization ($i = 0.1 \text{ A/cm}^2$) for 10 min

Electrolyte	$h, \mu\text{m}$	Phase composition	Elemental composition, at %						
			Ni	Cu	P	Al	O	W	Mg
PBW	12 ± 1	$\gamma\text{-Al}_2\text{O}_3$ AlPO_4	—	—	0.7	37.3	60.0	0.2	1.8
PBWNi	14 ± 1	$\gamma\text{-Al}_2\text{O}_3$ AlPO_4	4.8	—	0.8	37.4	54.8	0.2	1.8
PBWCu	18 ± 1	$\gamma\text{-Al}_2\text{O}_3$ AlPO_4	—	0.4	0.9	37.9	58.5	0.2	2.0
PBWNiCu	14 ± 1	$\gamma\text{-Al}_2\text{O}_3$	2.1	0.3	0.6	39.0	56.1	0.1	1.8

based on an analysis of published data. Thus, Dul'nev et al. [9] found that a catalytic activity maximum in redox reactions on supported nickel–copper catalysts was observed at the ratio $\text{NiO/CuO} = 2.3\text{--}3.0$.

The PEO layers were formed galvanostatically for 10 min at anodic polarization (effective current density $i_A = 0.05\text{--}0.10 \text{ A/cm}^2$) and anodic–cathodic polarization ($i_A = i_C = 0.10 \text{ A/cm}^2$; pulse durations $\tau_A = \tau_C = 0.02 \text{ s}$) using a computer-controlled reversible thyristor system. The solution temperature was no higher than 30°C .

The pretreatment of AMg5 aluminum alloy samples included chemical polishing in a mixture of concentrated acids $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4/\text{HNO}_3 = 4 : 2 : 1$ (by volume) at $110\text{--}120^\circ\text{C}$. The polished samples were washed with distilled water and dried in air at 70°C .

The thermal annealing of the samples with PEO coatings in a muffle furnace was performed in air under the following conditions: furnace heating to 500°C for about 1 h, exposure at the specified temperature for 2 h, and natural cooling of the furnace to room temperature for about 6 h.

The thickness of the layers was determined using an eddy-current thickness gauge. Data on the elemental composition and surface morphology were obtained on a JXA 8100 electron probe microanalyzer (Japan) with an INCA energy spectrum analyzer (United Kingdom). To prevent surface charging, graphite was sputtered onto the films before measurements. X-ray diffraction patterns were measured on a D8 Advance X-ray diffractometer (Germany) using $\text{CuK}\alpha$ radiation. X-ray diffraction analysis was performed with the use of the EVA retrieval program with the PDF-2 database.

X-ray photoelectron spectroscopy (XPS) was used for surface analysis. The XPS spectra were measured on a Specs ultrahigh-vacuum system using a 150-mm electrostatic hemispherical analyzer. Ionization was performed using $\text{MgK}\alpha$ radiation. The working vacuum was $2 \times 10^{-7} \text{ Pa}$. The spectra were calibrated against the C 1s lines of hydrocarbons, whose energy was taken equal to 285.0 eV .

Catalytic tests were performed using a BI-CATflow 4.2(A) multipurpose flow-type system (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). Finely cut wire samples of the AMg5 aluminum alloy with PEO coatings (the geometric surface area of the coating was 20 cm^2) were placed in the active zone (0.9 cm in diameter and 3 cm in height) of a quartz tube reactor. The initial reaction mixture contained 5% CO and air. The gas flow rate was 50 ml/min . The outlet concentrations of CO and CO_2 were determined using a PEM-2 IR gas analyzer. The test temperature range was $20\text{--}500^\circ\text{C}$.

RESULTS

The oxide layers prepared in the PBW electrolyte contained both alloying elements (magnesium) and elements from the electrolyte (phosphorus and tungsten) along with aluminum and oxygen (Table 1). The layers formed in the PBWNi, PBWCu, and PBWNiCu electrolytes contained nickel and/or copper in addition to the above elements.

The films contained $\gamma\text{-Al}_2\text{O}_3$ and AlPO_4 . Crystalline phases containing nickel and copper were not detected. According to X-ray spectroscopic and X-ray diffraction analysis data, the elemental and phase compositions of films remained unchanged upon annealing both in air and in a gas mixture of air + 5% CO during catalytic tests.

An analysis of the scanning electron micrographs of the surfaces of PEO layers (Fig. 1) allowed us to find the following relief peculiarities: Fused volcanolike formations were characteristic of all the films. Grain deposits can be seen on the fused surface of films formed in electrolytes with the nickel salt. As a rule, grains were arranged along the edges of fused formations or at the boundary between them. Apparent changes in the surface structure were not observed after catalytic tests and annealing in air.

According to XPS data (Table 2), Al^{3+} , Na^+ , O^{2-} , P^{5+} , Ni^{2+} , Cu^{2+} , Cu^+ , W^{6+} , and carbon were present on the surface of the test samples. Boron and magnesium were not detected on the surface. Carbon was present in

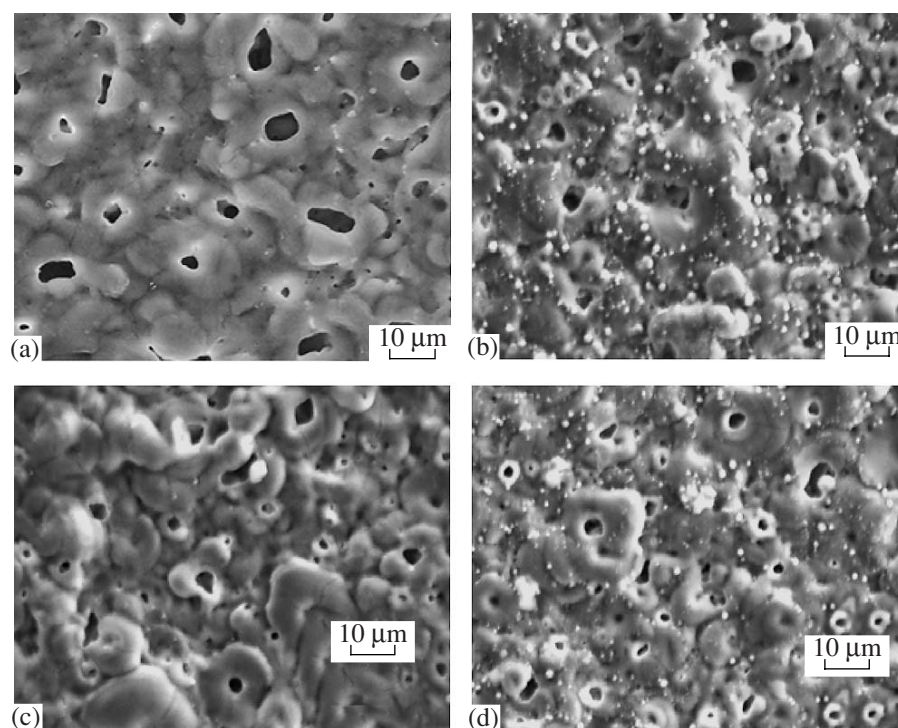


Fig. 1. Scanning electron micrographs of PEO layers formed on the AMg5 aluminum alloy by anodic polarization ($i = 0.10 \text{ A/cm}^2$) in the following electrolytes: (a) PBW, (b) PBWNi, (c) PBWCu, and (d) PBWNiCu.

various states. In particular, peaks corresponding to carbon bound to hydrogen C_{CH} and oxidized carbon C_{CO} can be recognized. The initial samples contained C_{CH} in a maximum amount. In addition, carbon bound to metal

C_{CM} was present in nickel- and nickel-copper-containing films.

In accordance with Table 2, samples containing various oxides exhibited the following changes in the ele-

Table 2. Concentrations of the elements in the surface layers of films formed in the PBWNi, PBWCu, and PBWNiCu electrolytes under galvanostatic conditions at $i = 0.10 \text{ A/cm}^2$ and $t = 10 \text{ min}$ according to XPS data

Elements	Coatings formed in electrolytes								
	PBWNi			PBWCu			PBWNiCu		
	initial	after annealing	after catalysis	initial	after annealing	after catalysis	initial	after annealing	after catalysis
Na	11.8	7.4	10.4	4.5	8.0	8.2	4.4	5.3	6.6
Cu, including:	—	—	—	8.4	10.9	11.2	5.4	6.7	4.9
Cu^{2+}	—	—	—	0.8	3.2	3.2	1.1	1.8	0.4
Cu^+	—	—	—	7.6	7.7	8.0	4.3	4.9	4.5
Ni	9.8	24.3	24.1	—	—	—	12.6	17.4	14.8
O	45.1	47.1	50.9	49.1	59.5	44.7	50.7	47.5	49.0
C	22.1	8.1	4.2	20.6	4.9	22.0	15.6	13.3	12.6
P	5.4	6.1	4.4	5.8	8.0	6.7	5.9	5.7	6.9
Al	5.6	6.8	5.8	11.4	8.0	6.7	5.2	3.8	4.9
W	0.2	0.2	0.2	0.2	0.7	0.5	0.2	0.3	0.3
Ni/Cu	—	—	—	—	—	—	2.33	2.60	3.02
Cu^{2+}/Cu	—	—	—	0.095	0.294	0.283	0.20	0.27	0.08

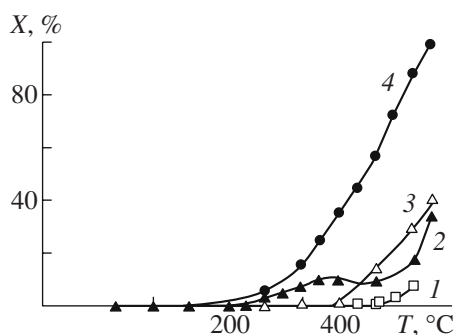


Fig. 2. Temperature dependence of the conversion of CO (X) for PEO layer/Al compositions formed by anodic polarization ($i = 0.10 \text{ A/cm}^2$) in the following nickel- and copper-containing electrolytes: (1) PBW, (2) PBWCu, (3) PBWNi, and (4) PBWNiCu.

mental composition of film surfaces upon thermal treatments (annealing and catalytic tests):

- In a nickel-containing sample, the concentration of Ni^{2+} noticeably increased, and the concentration of carbon decreased. In this case, the amount of C_{CH} decreased, whereas the amount of C_{CO} increased.

- In a copper-containing sample, the concentration of Cu^{2+} increased, and the concentration of Al^{3+} decreased. The amount of C_{CH} remained unchanged

after catalytic tests; however, it decreased after annealing in air. The concentration of C_{CO} increased. The concentration of W^{6+} increased after annealing in air and catalysis.

- In a nickel-copper-containing sample, the surface composition was least prone to changes under the action of high temperatures. Note that the amount of Ni^{2+} increased after annealing and the surface concentration of Cu^{2+} decreased after catalysis.

The PEO layers simultaneously containing nickel and copper compounds exhibited the highest catalytic activity (Fig. 2).

The temperature dependence of CO conversion for the nickel-containing samples remained unchanged upon repeated tests (Fig. 3a). The behavior of the curves was more complicated in the case of copper-containing samples (Fig. 3b). In particular, a plateau was observed in the first run, and this plateau was absent from the subsequent runs; the activity of the samples increased upon cooling (hysteresis). At the same time, in both cases, the annealing of the samples in air resulted in their deactivation (Figs. 3c, 3d).

Unlike the above samples, samples simultaneously containing nickel and copper compounds were more stable: they increased their activity in the course of consecutive catalytic tests (Fig. 4a) and did not lose it upon annealing in air (Table 3). Active samples were

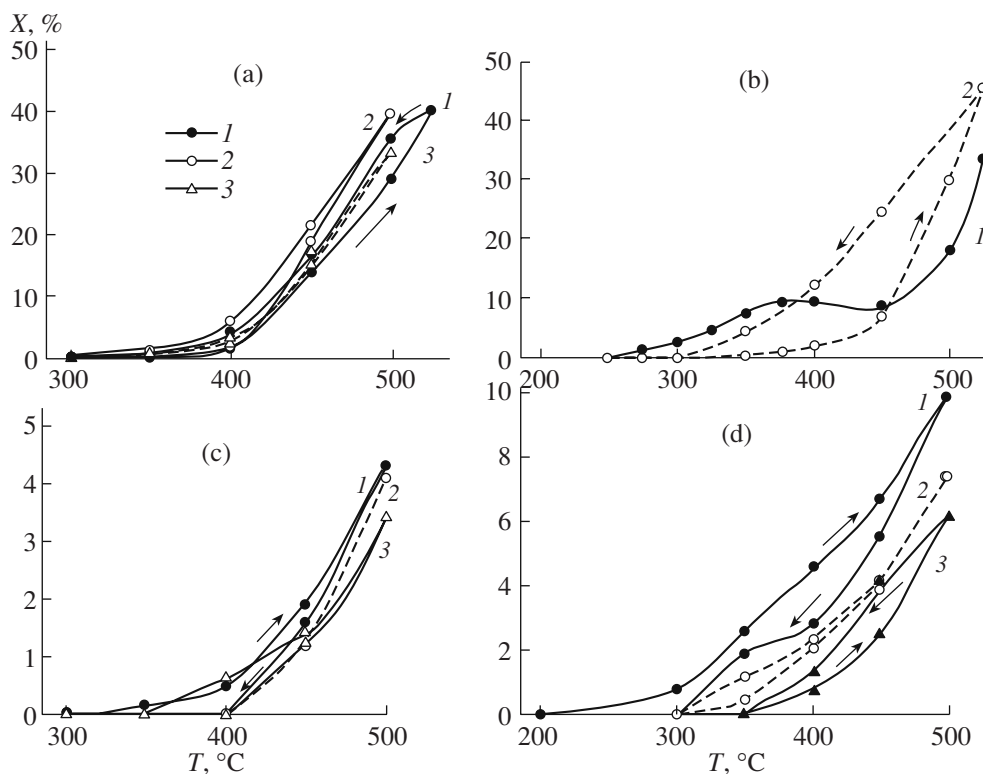


Fig. 3. Temperature dependence of the conversion of CO (X) for PEO layers formed on the AMg5 aluminum alloy in the (a, c) PBWNi and (b, d) PBWCu electrolytes by anodic polarization ($i = 0.10 \text{ A/cm}^2$; $t = 10 \text{ min}$) (a, b) before and (c, d) after preannealing in air. Numerals indicate consecutive heating and cooling cycles in catalytic tests.

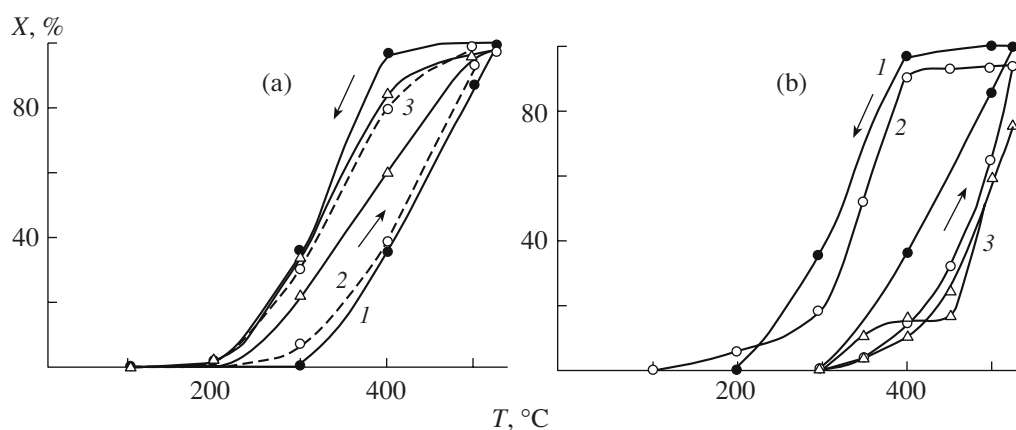


Fig. 4. Temperature dependence of the conversion of CO for the nickel–copper-containing samples formed (a) by anodic polarization ($i_A = 0.10 \text{ A/cm}^2$) (numerals indicate consecutive heating and cooling cycles in catalytic tests) and (b) by anodic ($i_A = (1) 0.10$ or (2) 0.05 A/cm^2) and (3) anodic–cathodic polarization ($i_A = i_C = \pm 0.10 \text{ A/cm}^2$).

obtained by both anodic polarization at various current densities and anodic–cathodic polarization (Fig. 4b). The use of anodic–cathodic polarization and annealing in air led to the same result: activity stabilization with a decrease in activity. Note that the films prepared at low current densities, as well as under conditions of alternating anodic–cathodic polarization, were less prone to chalking and flaking in bending, on impact, and at great temperature differences.

DISCUSSION

In accordance with X-ray spectroscopic analysis data, the oxygen content of the films was about 56 at % without regard for carbon (Table 1). According to XPS data, the oxygen content varied from sample to sample over the range 45–60 at % (Table 2). Because data obtained by both of the above techniques are similar, we can compare surface compositions (XPS) and volume-averaged data of the X-ray spectroscopic analysis of the films. This comparison showed that the concentration of aluminum on the film surface was noticeably lower than that in the bulk; at the same time, elements such as nickel, copper, sodium, and phosphorus were concentrated. Thus, the distribution of elements across film sections was inhomogeneous and elements from the electrolyte were concentrated on the surface.

Copper with the oxidation numbers 2+ and 1+ occurred on the film surfaces, whereas the electrolyte contained bivalent copper acetate. The reduction of copper can be associated with the effect of hydrogen, which was detected as a constituent of gas released at the anode in the PEO process [14]. Because nickel is a more active metal, the reduction of copper rather than nickel took place. Dul'nev et al. [9] also found that the temperature-programmed reduction of CuO bound to an inert support ($\alpha\text{-Al}_2\text{O}_3$) with hydrogen occurred at lower temperatures (330–360°C) than those in the case of NiO (450–470°C).

All of the samples contained considerable amounts of carbon (Table 2). It is likely that the reason for the appearance of carbon in the surface layer is the presence of acetate ions (whose constituents are both methyl and carboxyl groups) in solution. Note that carbon bound to metal (C_{CM}) was present in the samples with nickel. This is likely due to the fact that iron subgroup metals are prone to carbide formation, and finely dispersed nickel particles can catalyze the formation of carbon nanofibers, for example, under conditions of hydrocarbon (in particular, methane) conversions in the temperature region 400–600°C [15]. In this context, note the occurrence of grain deposits on the surface of nickel-containing samples (Fig. 1). It is likely that the grains are carbon-containing formations.

The annealing of samples in air resulted in the burning of a portion of carbon in all cases. Because the major portion of carbon was of organic origin, it is likely that carbon was oxidized to gaseous carbon oxides because of high-temperature interaction with atmospheric oxygen. Only in the case of nickel–copper-containing samples was the decrease in the concentration of carbon insignificant.

Table 3. Effect of the conditions of preparation of nickel–copper-containing layers on the temperature of 50% CO conversion

Preparation conditions		$T_{50}, ^\circ\text{C}$	
		heating	cooling
Anodic polarization	$i_A = 0.10 \text{ A/cm}^2$	430	330
	$i_A = 0.05 \text{ A/cm}^2$	480	350
Anodic–cathodic polarization	$i_A = i_C = 0.10 \text{ A/cm}^2$	490	435
Anodic–cathodic polarization + annealing		515	470

As can be seen in Fig. 3, the activity of nickel- and copper-containing samples was retained upon high-temperature interactions with a reaction gas mixture in the course of catalytic tests. However, the samples were almost deactivated after annealing in air at the same temperatures. At the same time, it is difficult to relate activity changes to surface composition changes based on the experimental data (Table 2). It is believed that the occurrence of solid-phase agglomeration processes and the formation of mixed oxides (aluminates, whose activity in CO oxidation reactions is lower than that of individual copper and nickel oxides) in a coating layer is responsible for deactivation upon annealing in air. The probability of agglomeration can increase in an oxidizing atmosphere (on annealing in air), whereas the presence of CO in the reaction mixture hinders this process.

Unlike the copper- and nickel-containing samples, the nickel-copper-containing samples did not deactivate upon annealing in air and their surface composition remained unchanged. The mechanism of a synergistic effect of copper and nickel, as well as the nature of copper and nickel compounds in the films (hypothetically, oxides), is unclear. The higher activity of binary nickel-copper oxide systems was related to the promoting effect of copper [10] and to the formation of solid solutions in the NiO-CuO system [10] and nickel cuprate [8, 16], which prevents nickel and copper oxides from dissolving in the substrate. In the course of repeated catalytic tests, an increase in the activity of the samples was observed. In this case, as can be seen in Table 2, the concentration of Cu^{2+} on the film surface decreased after catalytic tests at a constant concentration of Cu^+ ; in other words, the fraction of monovalent copper on the surface increased. It is well known [17] that samples containing Cu^+ were more active than samples with Cu^{2+} .

Annealing in air, as well as the use of anodic-cathodic polarization, resulted in a decrease in activity with the simultaneous stabilization of catalytic properties, in particular, in a decrease in hysteresis in the CO conversion-temperature curve (Fig. 4). Evidently, this is due to the fact that influences of this kind, for example, anodic-cathodic treatment [18, 19], enhanced the thermal stability and compositional homogeneity of films.

Note that the surface structures formed by the PEO process exhibit a relatively low specific surface area (about 0.2–0.7 m^2/g , as estimated by Patcas and Krysmann [6]), which suggests sufficiently high catalytic activity of a unit surface of the synthesized nickel-copper-containing films in CO oxidation. An analogous conclusion was also made with respect to nickel-, chromium-, and molybdenum-containing PEO layers on aluminum, titanium, and magnesium in the oxidative dehydrogenation of cyclohexane [6].

CONCLUSIONS

Thus, oxide layers containing $\gamma\text{-Al}_2\text{O}_3$ and nickel and copper compounds, which catalyze CO oxidation to 30°C over the temperature region 300–500 $^\circ\text{C}$, were prepared on aluminum using PEO in an aqueous electrolyte with an average temperature of no higher than 30°C . The surface composition and catalytic characteristics of the films were stable under thermal exposures in both air and a gas mixture of air + 5% CO. Elements such as nickel, copper, sodium, and phosphorus from the electrolyte were concentrated on the film surfaces. Nickel occurred as Ni^{2+} , whereas copper occurred as Cu^+ and Cu^{2+} . The $\text{Ni}^{2+}/(\text{Cu}^+ + \text{Cu}^{2+})$ on the surface was 2.3–3.0; the major portion of copper occurred in the state Cu^+ . The surface contained noticeable amounts of carbon. Formation by anodic-cathodic polarization and annealing in air resulted in a decrease in catalytic activity with the stabilization of the composition and an increase in the mechanical resistance of the compositions. Along with published data [5, 6], the results obtained in this work demonstrated that the PEO process is promising for the manufacture of catalysts supported on metal substrates, which are active in various reactions.

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